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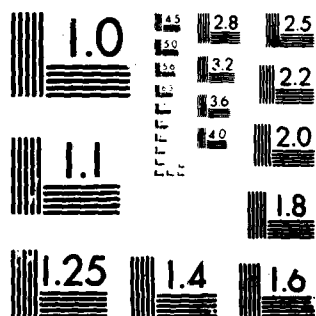3-80
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Surface-Hopping Model for Near-Resonant
Electronic Energy Transfer

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Interim Report

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This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

Gerhard E. Aichinger
Project Officer

FOR THE COMMANDER

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A surface-hopping model was developed to account for the large near-resonant electronic energy transfer cross sections in systems such as NF-Bi and O_2-I, in which the dipole-dipole mechanism is formally forbidden. Multiple surface crossings are predicted to occur in NF-Bi at distances of ≈ 8 Å, because of long-range (R^{-5}) dipole-induced dipole terms in the potential. This corresponds well with the measured transfer cross section of ≈ 200 Å^2. These terms are absent in O_2-I, so that the leading

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ABSTRACT (Continued)

approximately 3.5 Å

term is the London dispersion interaction with an R dependence of R^{-6}. The predicted crossing distance is ≈ 3.5 Å, in agreement with the smaller transfer cross section for this system. A Landau-Zener crossing probability is used to predict the temperature dependence of the thermally averaged cross section $Q(T)$ for the I-atom laser pumping reaction,

$$O_2*(a^1\Delta) + I(^2P_{3/2}) \longrightarrow O_2(X^3\Sigma_g^-) + I*(^2P_{1/2})$$
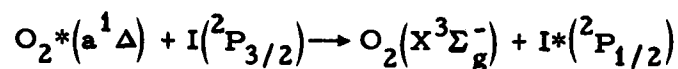
Requirements for a more accurate calculation are discussed.

PREFACE

CONTENTS

FIGURES

I. INTRODUCTION

A recent measurement[1] of the rate for the near-resonant electronic energy-transfer reaction

$$Bi\left({}^4S_{3/2}\right) + NF*(a^1\Delta) \longrightarrow Bi*\left({}^2D_{3/2}\right) + NF(X^3\Sigma)\,(\Delta E = 16\ cm^{-1}) \qquad (1)$$
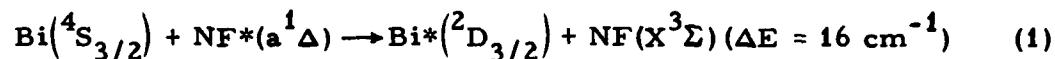
has yielded a value of $1 \times 10^{-9}\ cm^3\ molecule^{-1}\ sec^{-1}$, corresponding to a thermally averaged cross section $\approx 200\ \mathring{A}^2$, which is much greater than gas kinetic. The theoretical problem posed by this result is that the electronic transitions involved in this process are both strongly dipole forbidden $(A_{21} = 31$ and $1\ sec^{-1}$ for the Bi and NF transitions, respectively). Thus, the model of interacting transition dipoles, usually employed for such processes, cannot account for the observed efficiency. In this report, we discuss an alternative model, based on potential surface crossings at large interparticle distances, which successfully accounts for the observed rate.

An understanding of these processes is important for several reasons. Transfer reactions, e.g., Reaction (1), are the basis for the recently developed metastable transfer emission spectroscopy technique,[2] which is a powerful method for determining trace components in gas mixtures.[3] A similar reaction,

$$I\left({}^2P_{3/2}\right) + O_2*(a^1\Delta) \longrightarrow I*\left({}^2P_{1/2}\right) + O_2\left(X^3\Sigma_g^-\right)(\Delta E = 279\ cm^{-1}) \qquad (2)$$
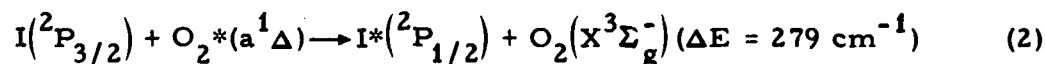
is the basis for the chemically pumped O_2-I transfer laser.[4] In order to optimize the performance of this system and analogous potential laser systems, it is necessary to be able to model the dependence of the key transfer step, Reaction (2), on such parameters as energy defect, reactant states, and gas temperature.

The inadequacy of the transition dipole-dipole interaction mechanism was previously pointed out by Breckenridge and co-workers[5] for the case of Cd*-NO and Zn*-NO energy transfer. They suggested an alternative mechanism, such as direct or charge-transfer curve crossing, as an explanation. A similar model has been proposed by Setser and co-workers[6] for quenching of metastable rare-gas atoms. In this report, NF*-Bi and O_2*-I transfer processes are discussed in terms of a mechanism of this type.

II. SURFACE CROSSINGS IN NF*-Bi

The electronic energy levels associated with the low-lying states of Bi and NF are shown schematically in Fig. 1. These states will effect a variety of triatomic potential surfaces at small Bi-NF distances; in addition, a strongly attractive surface will result from the $Bi^+ - NF^-$ charge-transfer state. This attractive ionic surface will cut through the neutral surfaces arising from $Bi(^4S) + NF(^1\Delta)$ and $Bi(^2D) + NF(^3\Sigma)$ at a Bi-NF separation R_o given by

$$U(R_o) = [I. P. (Bi) - E.A. (NF)] - E_{exc} \tag{3}$$

where I.P. is ionization potential, E.A. is electron affinity, and E_{exc} is the energy of the electronically excited levels (1.42 eV). The interaction potential U(R), in this point-charge approximation, includes contributions from both coulomb attractive and charge-induced-dipole terms, and, thus is given by

$$U(R) = -\frac{e^2}{R} - \frac{e^2\alpha}{R^4} \tag{4}$$

In order to find R_o, we need to know the ionization potential of bismuth, the electron affinity of NF, and the polarizability α of the most polarizable species in the system, which will be the negative ion NF^-. The ionization potential of Bi is known spectroscopically[7] to be 7.28 eV, but the other two quantities are not experimentally determined. An ab initio calculation[8] gives E.A. (NF) $\simeq 0.6$ eV; we accept this value because the ionization potential of NF, calculated from the same wave functions, is 13.2 eV, in excellent agreement with the experimental value (13.1 eV).[9] The polarizability of
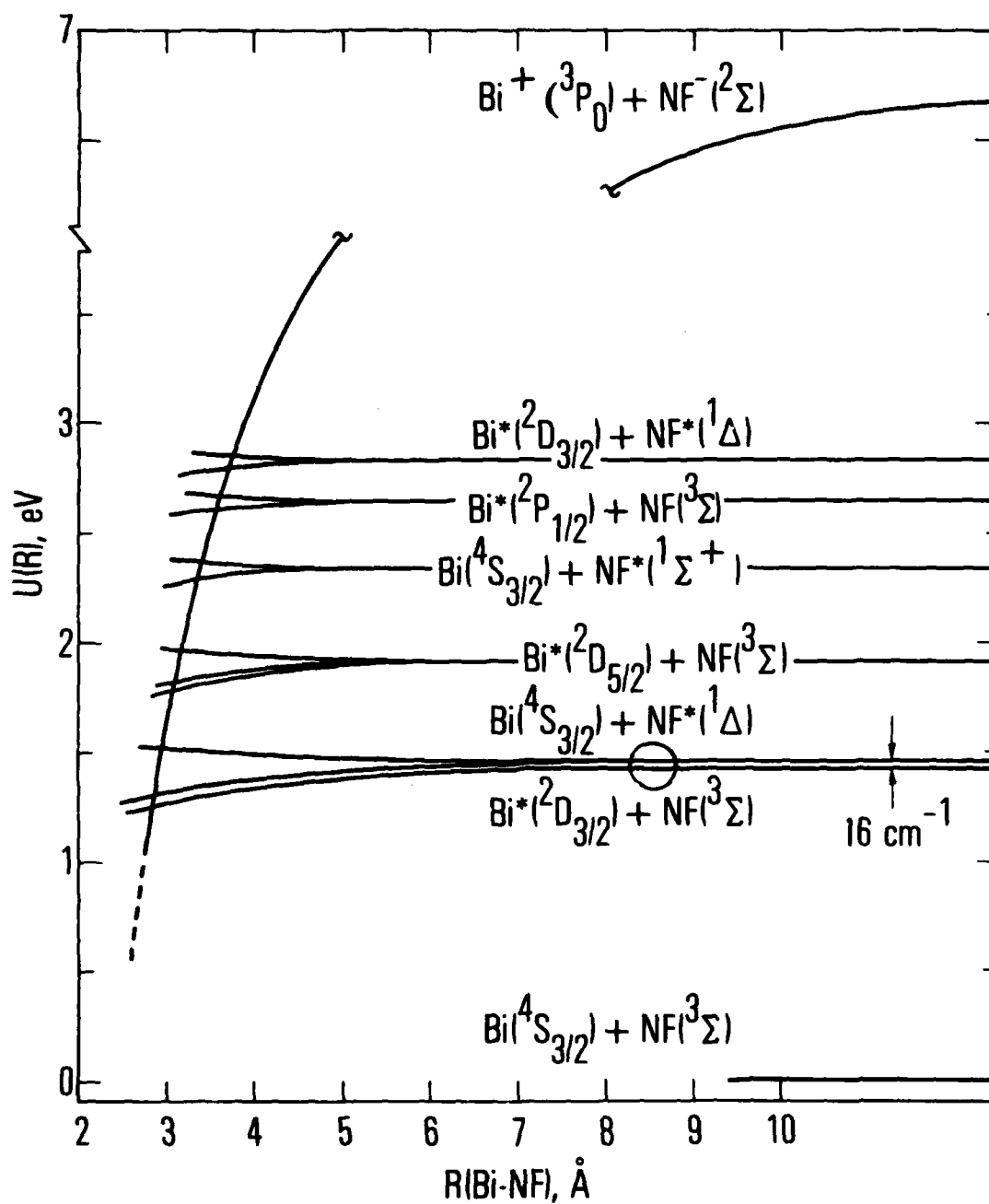
Fig. 1. Low-Lying Electronic States of Bi and NF and Attractive Curve Resulting from Interaction of Bi$^+$ and NF$^-$

NF^- is taken to be slightly larger than that of O_2,[10] i. e., 2×10^{-24} cm^3. Combining Eqs. (3) and (4), we obtain

$$- \frac{e^2}{R_o} - \frac{e^2 \alpha}{R_o^4} = 7.28 - 0.6 - 1.42 \text{ eV}$$

$$= 5.26 \text{ eV}$$

$$= 8.43 \times 10^{-12} \text{ erg}$$

The required value of R_o is 2.95 Å, which is much too small to account for the observed efficiency of Reaction (1). The corresponding cross section, 27 Å^2, is nearly an order of magnitude smaller than the measured cross section. Thus, the charge-transfer surface cannot be important in the non-adiabatic surface-crossing process, and we focus attention instead on the direct crossing of the two surfaces correlating with $NF^*(a^1\Delta) + Bi(^4S_{3/2})$ and with $NF(X^3\Sigma)$ and $Bi^*(^2D_{3/2})$.

A schematic representation of these surfaces, at a fixed N-F distance, is shown in Fig. 2. The symmetries of the intermediate nonlinear Bi-NF complexes must be determined from adiabatic correlation rules.[11] Since the heavy atoms are in a j-coupled limit (only one spin-orbit component interacts with each molecular state), Hund's Case C coupling is appropriate for the complex. For $Bi(^4S_{3/2}) + NF(^1\Delta)$, $^4A'$ and $^4A''$ surfaces will be obtained. The $Bi(^2D_{3/2}) + NF(^3\Sigma)$ interaction will result in $^4A'$, $^4A''$, $^2A'$, and $^2A''$ states. Thus, multiple surface crossings are possible. Attention is focused on one possible crossing, shown in Fig. 2, in order to estimate the crossing distance R_o.

The leading term in the long-range potential between these two species will be the dipole-induced-dipole interaction,

U(R), cm^{-1}

11,435 —

11,419 —

$^4A''$, Bi($^4S_{3/2}$) + NF*(a$^1\Delta$)

$^4A'$

16 cm^{-1}

$^4A'$, $^4A''$, $^2A'$, $^2A''$

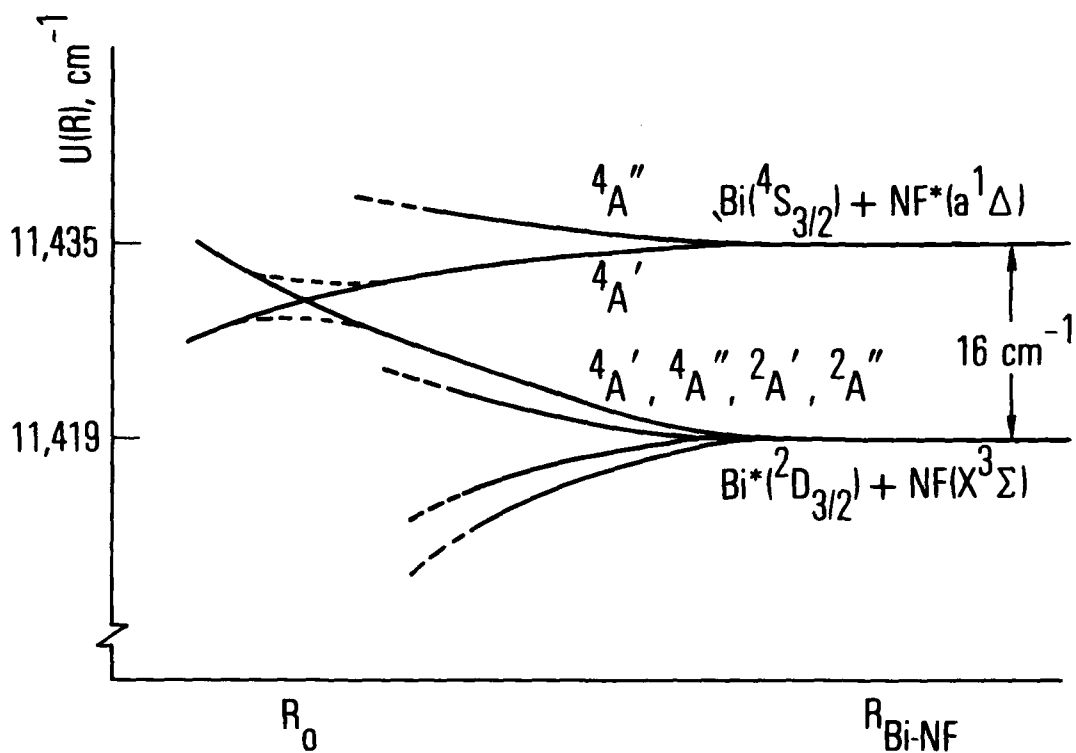Bi*($^2D_{3/2}$) + NF(X$^3\Sigma$)

R_0

R_{Bi-NF}

Fig. 2. Avoided Crossing of Bi-NF* and Bi*-NF Potential Surfaces. The adiabatic surface sections, shown as dotted lines, lie in the region indicated by the circle in Fig. 1.

$$U(R) \simeq \frac{e\mu(NF)\alpha(Bi)}{R^5} \tag{5}$$

The dipole moments and polarizabilities are needed for both the NF and Bi ground and electronically excited states. We take $\alpha(Bi)$ [Z = 83] $\simeq 2 \times \alpha(I)$ [Z = 53] $\simeq 2 \times (5.1 \times 10^{-24} cm^3)^{12} \simeq 10^{-23}$ cm^3 and $\alpha(Bi*) \simeq 3 \times \alpha(Bi) \simeq 3 \times 10^{-23}$ cm^3.[13] The dipole moment of $NF(a^1\Delta)$ has been measured[14] to be 0.37 D = 3.7×10^{-19} esu-cm. The previously cited calculation[8] gives $\mu(NF^3\Sigma) - \mu(NF^1\Sigma) = 0.24$ D. We, thus, take $\mu(NF^3\Sigma) \simeq 6.1 \times 10^{-19}$ esu-cm (the experimental value is not known). With the use of these values, R_o was estimated from

$$\frac{e}{R^5} (\mu*\alpha + \mu\alpha*) = 16 \text{ cm}^{-1}$$

$$= 3.18 \times 10^{-15} \text{ erg}$$

where the * refers to the property of the electronically excited species. With the above values, it is found that $R_o \simeq 8$ Å, corresponding to a cross section of 200 Å^2.

The agreement of this calculated value with the experimental one (200 Å^2) is, of course, fortuitous. Most of the parameters used to determine this value are rough estimates, and the experimental value itself has an error bracket of ±50%. Nevertheless, the fact that the two numbers are the same indicates that the basic model for the process is essentially correct. This model also accounts satisfactorily for the roughly five times smaller rate for the similar exchange process[15]

$$I*\left(^2P_{1/2}\right) + NF(a^1\Delta) \longrightarrow I\left(^2P_{3/2}\right) + NF*(b^1\Sigma^+) \, (\Delta E = 110 \text{ cm}^{-1}) \tag{6}$$
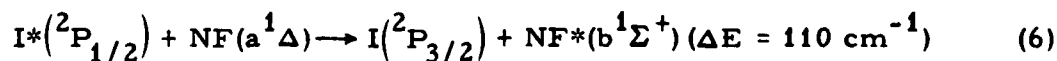
The explanation is simply that the larger energy defect in Reaction (6) results in a smaller crossing distance R_o and a correspondingly smaller transfer cross section.

III. NEAR-RESONANT ELECTRON ENERGY TRANSFER
IN O_2^*-I SYSTEM

The successful demonstration of the O_2^*-I transfer laser system[4] has provided a strong motivation for understanding near-resonant electronic energy-transfer processes, such as the excitation transfer, Reaction (2). A model for this process similar to that employed for the NF*-Bi system is considered, and Landau-Zener theory is then used to estimate a temperature dependence for the rate of this reaction.

A.   POTENTIAL SURFACE CROSSINGS

The electronic energy levels associated with the low-lying states of I and O_2 are shown schematically in Fig. 3. As in the NF*-Bi case treated earlier, a charge-transfer surface (arising from I^- and O_2^+) will intersect the neutral surfaces (arising from I* + O_2, I + O_2^*). The crossing distance R_o is estimated from Eqs. (3) and (4), with I.P. (O_2) = 12.06 eV,[16] E.A. (I) = 3.06 eV,[17] and E_{exc} = 0.94 eV [since I.P. (I) = 10.45 eV,[7] and E.A. (O_2) = 0.5 eV,[16] the surface arising from $I^+ + O_2^-$ lies $\approx$ 1 eV above that from $I^- + O_2^+$, and thus intersects the I*-O_2 surfaces at an even smaller R_o]. The polarizability of I^- is 6.2 $\mathring{A}^3$.[18] Thus, we have

$$\frac{e^2}{R_o} - \frac{e^2 \alpha}{R_o^4} = 12.06 - 3.06 - 0.94 \text{ eV}$$

$$= 8.06 \text{ eV}$$

$$= 1.29 \times 10^{-11} \text{ erg}$$

or a value of R_o = 2.5 $\mathring{A}$. Whereas this does yield an estimate of the cross section for Reaction (2) in agreement with the experimental value[19-21] of 15 $\mathring{A}^2$, it is more likely that the process is dominated by the direct surface crossing at larger R_o, as shown in Fig. 3.
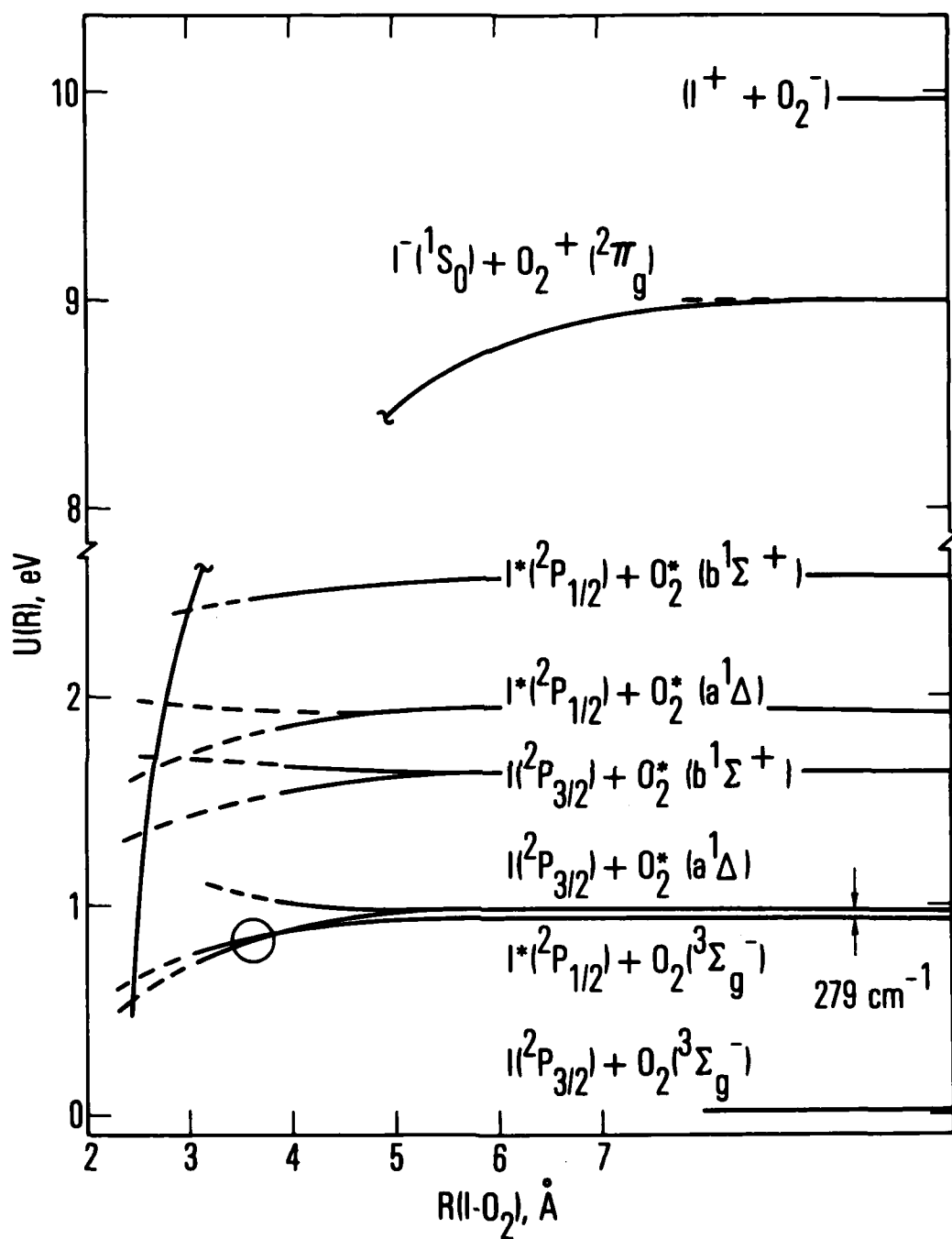
Fig. 3. Low-Lying Electronic States of I and O_2 and Attractive Curve Resulting from Interaction of I^- and O_2

-14-

For $I + O_2$, none of the species has a permanent dipole moment, so that the leading term in the long-range interaction is the London dispersion energy[17]

$$U_{AB}(R) = -\frac{3}{2} \frac{(IP)_A (IP)_B}{(IP)_A + (IP)_B} \frac{\alpha_A \alpha_B}{R^6} \qquad (7)$$

From the adiabatic correlation rules,[11] it is found that the interaction of $I*\left(^2P_{1/2}\right)$ with $O_2\left(^3\Sigma_g^-\right)$ results in $^4A'$ and $^2A'$ surfaces, whereas $I\left(^2P_{3/2}\right) + O_2^*\left(a^1\Delta_g\right)$ results in several $^2A'$ and $^2A''$. Thus, the avoided crossing will be between surfaces of $^2A'$ symmetry. A suggested model for the crossing region is shown in Fig. 4.

The surface sections $U_1(R)$ and $U_2(R)$, shown in Fig. 4, are given by Eq. (7), with the appropriate molecular parameters. In order to find the required ionization potentials, it is necessary to subtract the correct excitation energy; thus,

$$\text{I. P. } (O_2^*) = \text{I. P. } (O_2) - E(a^1\Delta)$$

$$= 12.06 \text{ eV}^{15} - 0.98 \text{ eV} = 11.08 \text{ eV}$$

and

$$\text{I. P. } (I*) = \text{I. P. } (I) - E\left(^2P_{1/2}\right)$$

$$= 10.45 \text{ eV}^7 - 0.94 \text{ eV} = 9.51 \text{ eV}$$

The polarizability of O_2 is $1.6 \times 10^{-24} \text{ cm}^3$;[10] we take $\alpha(O_2^*) \simeq 2\alpha(O_2) \simeq 3.3 \times 10^{-24} \text{ cm}^3$.[13] The polarizability of an I atom is $5.1 \times 10^{-24} \text{ cm}^3$.[12]
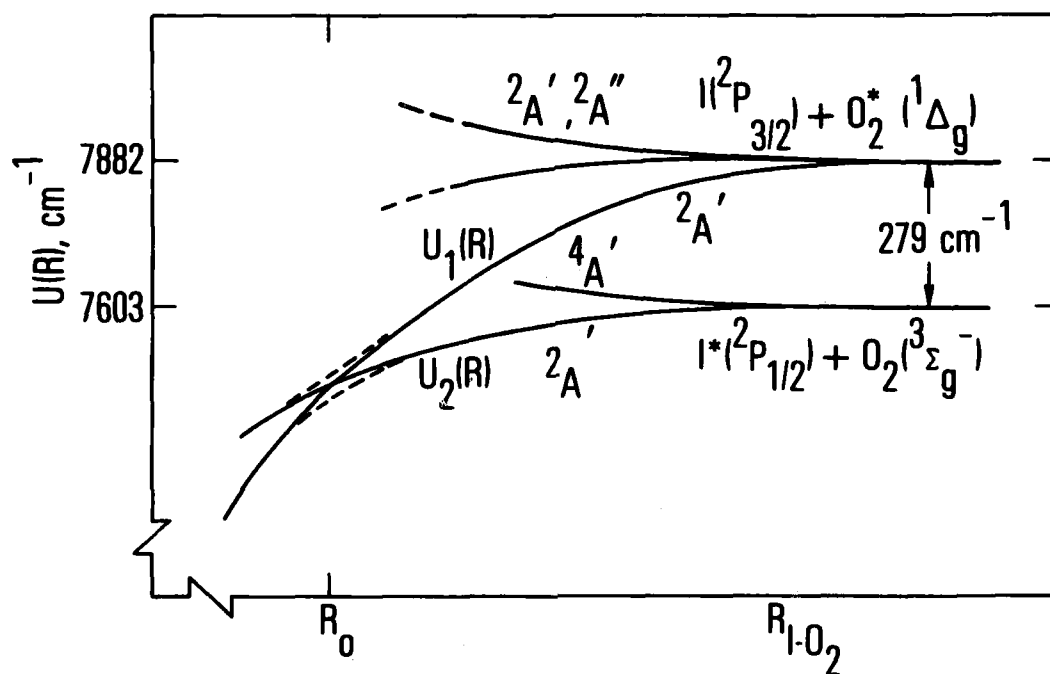
Fig. 4. Avoided Crossing of I-O$_2$* and I*-O$_2$ Potential Surfaces.
The adiabatic surface sections, shown as dotted lines,
lie in the region indicated by the circle in Fig. 3.

Since the $^2P_{1/2}$ state is a spin-orbit component with the same configuration as the ground $\left(^2P_{3/2}\right)$ state, we take $\alpha(I^*)$ only slightly larger than $\alpha(I)$, viz., 6×10^{-24} cm^3. These choices give

$$U_1(R) = - \frac{1.095 \times 10^{-42} \text{ cm}^{-1}}{R^6} \tag{8a}$$

and

$$U_2(R) = - \frac{6.17 \times 10^{-43} \text{ cm}^{-1}}{R^6} \tag{8b}$$

with R in cm. To find R_o^2, we set $U_1(R_o) = U_2(R_o) + 279$ cm^{-1}, which gives $R_o = 3.45$ Å. The cross section πR_o^2 is, thus, 37.4 Å^2, compared to the experimental value[19-21] of (15 ± 5)Å^2. A more precise comparison of this model with experiment requires the use of Landau-Zener theory for the actual surface-crossing efficiency, which is discussed in the following section.

B. **CALCULATION OF MAGNITUDE AND TEMPERATURE DEPENDENCE OF EXCITATION TRANSFER PROBABILITY IN I + O$_2$***

The Landau-Zener model[22,23] has been widely used to calculate non-adiabatic curve-crossing probabilities in molecular collisions. Several reformulations of the model have recently been presented;[24,25] the model has also been compared with the method of analytic continuation across a crossing seam.[26] The quantities pertinent to this model are defined in Fig. 5. "Splitting" of the adiabatic surfaces in the vicinity of R_o is identified as V_{12}. As the system approaches on surface 1, the probability of remaining on that surface is given by
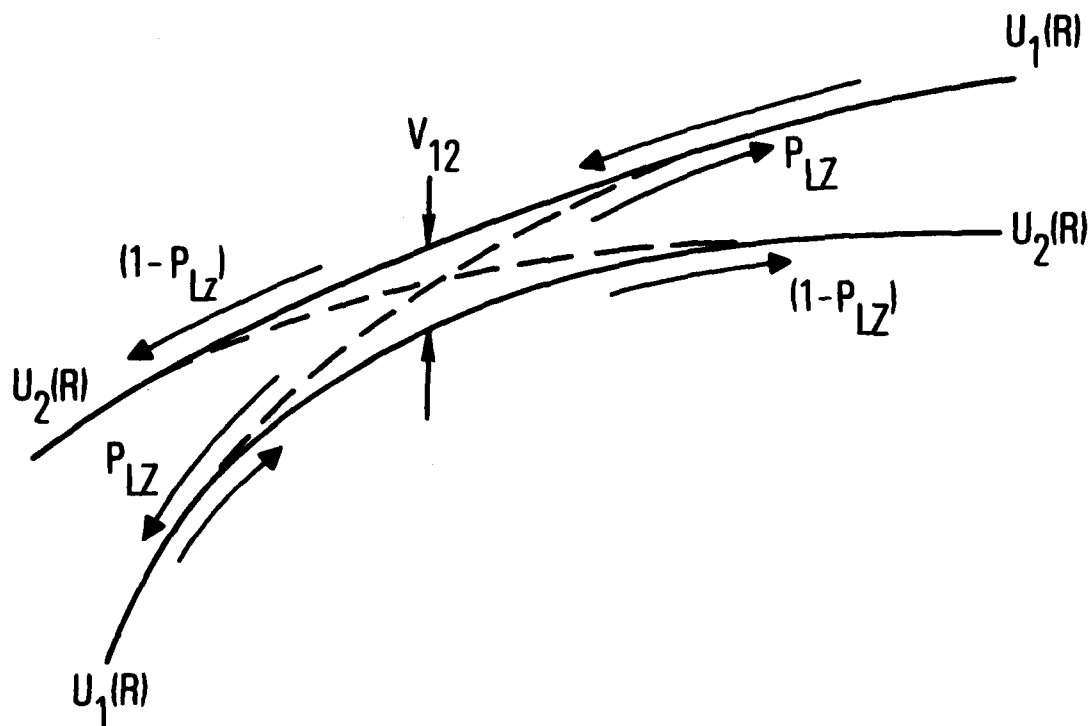
Fig. 5. Definitions of Quantities Required in Landau-Zener
Calculation

$$P_{LZ} = \exp\left(-\frac{2\pi |V_{12}|^2}{h \, |U_1' - U_2'| \, v}\right) \tag{9}$$

where $U_1' = dU_1(R)/dR\big|_{R=R_o}$, $U_2' = dU_2(R)/dR\big|_{R=R_o}$, and v is the relative velocity of the colliding species (I and O_2, in this case). Since a net transition from surface 1 to surface 2 requires two traversals of the region shown in Fig. 5, with the system "crossing" on one passage and following the adiabatic surface on the other, the net probability of excitation transfer is

$$P_{12}(v) = 2P_{LZ}(1 - P_{LZ}) \tag{10}$$

The thermally averaged transfer cross section is then

$$Q(T) = \pi R_o^2 \, \frac{\int P_{12}(v) \, f(v) \, v \, dv}{\int f(v) \, v \, dv} \tag{11}$$

with $f(v)$ given by the Maxwell-Boltzmann velocity distribution,

$$f(v) \, dv = 4\pi \left(\frac{\mu}{2\pi kT}\right)^{3/2} \exp\left(-\frac{\mu v^2}{2kT}\right) v^2 \, dv \tag{12}$$

For the O_2-I system considered here, with $U_1(R)$ and $U_2(R)$ given by Eqs. (8a, b), $U_1' = 2.43 \times 10^{-5}$ dyn, $U_2' = 1.40 \times 10^{-5}$ dyn, so that $|U_1' - U_2'| \simeq 10^{-5}$ dyn, evaluated at $R_o = 3.45 \times 10^{-8}$ cm. Since there is no value for V_{12}, estimates of 10, 30, and 100 cm^{-1} are used (i.e., of the order of the London dispersion interaction itself). The reduced mass μ of the I-O_2 collision pair is 4.24×10^{-23} g.

The results of a numerical integration of Eq. (11) are shown in Fig. 6. It is clear that a value of $V_{12} \simeq 30 \, cm^{-1}$ gives the correct magnitude for the cross section, whereas estimates much above or much below this figure lead
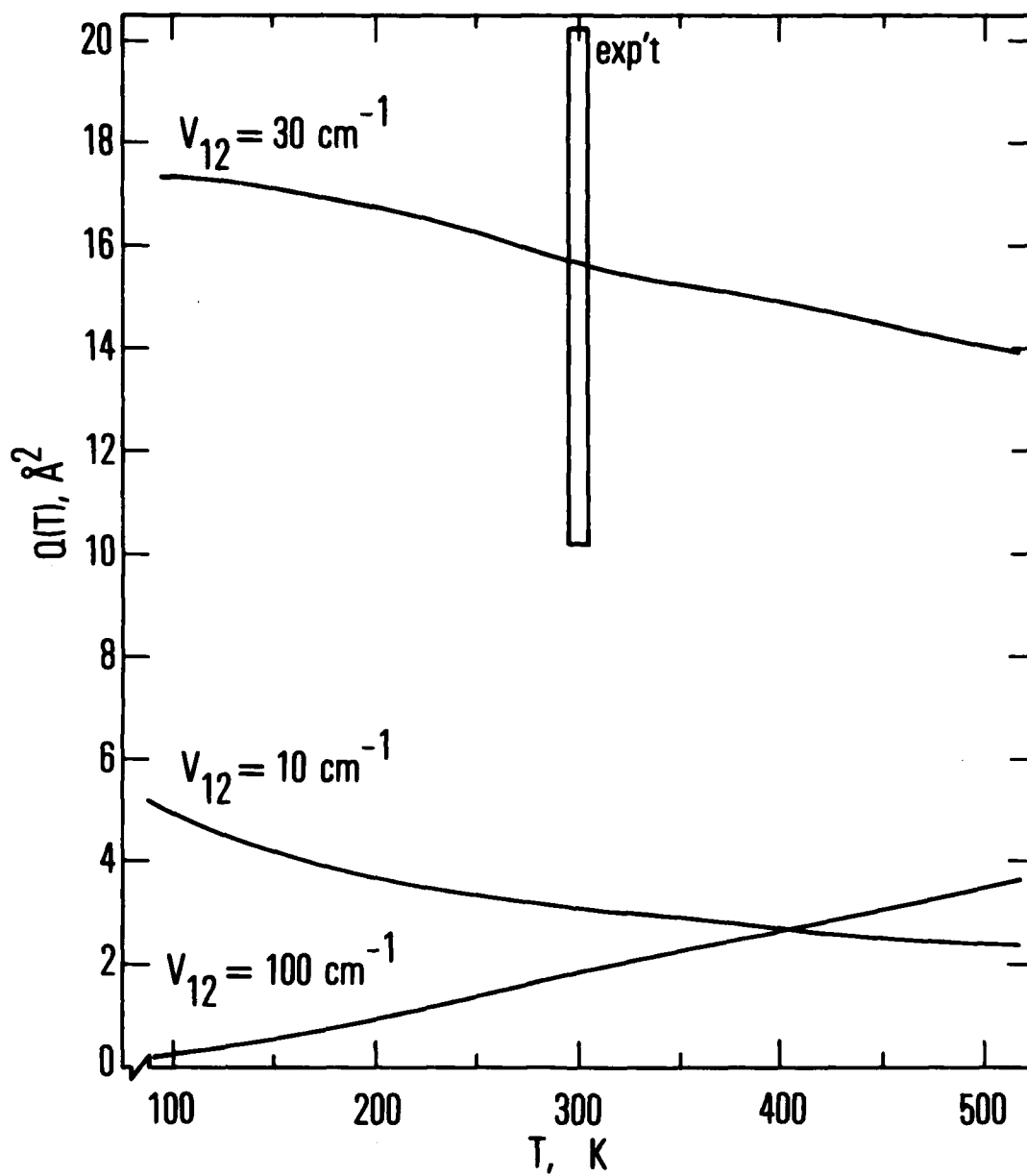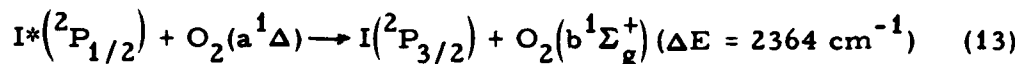
Fig. 6. Temperature Dependence of Thermally Averaged Cross
Section Q(T) for O_2^*-I Excitation Transfer

to gross underestimates. The temperature dependence predicted by this model is particularly striking. The temperature variation in Q(T) over the entire temperature range, 100 to 500 K, is smaller than the stated uncertainty in the measured value[19-21] at 300 K. Thus, before embarking on an experimental program designed to measure this temperature dependence, it would be advisable to reduce the experimental uncertainties in the room-temperature measurement, in order to obtain meaningful results.

The performance of the O_2-I transfer laser is a function of the excitation transfer reaction, Reaction (2), and the quenching reaction

$$I*\left(^2P_{1/2}\right) + O_2\left(a^1\Delta\right) \longrightarrow I\left(^2P_{3/2}\right) + O_2\left(b^1\Sigma_g^+\right) (\Delta E = 2364 \text{ cm}^{-1}) \quad (13)$$

The rate of this reaction is reported[20, 21] to be $k_{13} = 1.6 \times 10^{10}$ cm^3 mole^{-1} sec^{-1}, or $Q(300 \text{ K}) \simeq 5 \times 10^{-19}$ cm^2. Whereas a calculation similar to the foregoing could be attempted for the quenching cross section, the many uncertainties in the required molecular parameters would make the calculation of such a small cross section of doubtful significance. Qualitatively, it is found that cross sections of this type, with magnitudes much less than 1 Å^2, are steeply rising functions of temperature.[27] Thus, it is suspected that the efficiency of the O_2-I transfer laser will be improved by operation at reduced temperatures, with the small increase in the transfer cross section (shown in Fig. 6) being accompanied by a much larger relative decrease in that for the quenching reaction, Reaction (13).

IV. REFINEMENTS TO MODEL

In this report, a simple surface-crossing model is discussed, which accounts, at least qualitatively, for the efficiencies of such near-resonant electronic-energy-transfer processes as the excitation of Bi by NF*, Reaction (1), or of I by O_2*, Reaction (2). A more exact quantitative treatment would involve integration of classical collision trajectories on an assumed set of potential surfaces, with the probability of crossing from one electronically adiabatic surface to another given by a Landau-Zener, Eq. (9), or equivalent expression. Such surface-hopping trajectory calculations have been successfully carried out for such systems as $H^+ + H_2$,[27] $H^+ + D_2$,[28] I_2 + rare gas ($\rightarrow$ 2I + rare gas),[29,30] $N_2(B^3\Pi_g)$ + Ar $[\rightarrow N_2(W^3\Delta_u)$ + Ar],[31] and He_2^+ + Ne.[32] In order to describe such energy-transfer processes as Reactions (1) or (2), a surface-hopping inelastic trajectory calculation would have to be carried out. For such a calculation to be meaningful, much more accurate potential surfaces will be required than the simple models that were used in this study. Such surfaces can, in principle, be constructed by a method such as that of diatomics in molecules.[33] If such surfaces, along with improved accuracy in experimental measurements of these rates, were available, then a calculation of these rates by surface-hopping inelastic trajectories would be warranted.

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13. The polarizabilities of electronically excited atoms or molecules are frequently much larger than those of the ground-state species. For example, the polarizability of $Ar\left({}^1S_0\right)$ is 1.64×10^{-24} cm^3 [A. Dalgarno and A. E. Kingston, Proc. R. Soc. of London, A259, 424 (1961)], whereas that for $Ar^*\left({}^3P_2\right)$ is 48.4×10^{-24} cm^3 [B. Bederson and E. J. Robinson, "Molecular Beams," Adv. Chem. Phys. 10, and J. Ross, ed., Interscience Publishers, New York (1966), p. 25]. Thus, the estimate of $\alpha(Bi^*) \simeq 3 \times \alpha(Bi)$ is a conservative one.

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